Synthetic Polymer-Based Sensors

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Polymers are long-chain, highly molecular weight molecules containing large numbers of repeating units within their backbone derived from the product of polymerization of monomeric units. The materials exhibit unique properties based on the types of bonds that exist within their structures. Among these, some behave as rubbers because of their excellent bending ability, lightweight nature, and shape memory. Moreover, their tunable chemical, structural, and electrical properties make them promising candidates for their use as sensing materials. Polymer-based sensors are highly utilized in the current scenario in the public health sector and environment control due to their rapid detection, small size, high sensitivity, and suitability in atmospheric conditions.

Keywords: shape memory ; polymer-based sensors ; Synthetic

1. Polymers Using Molecular Imprinting (MIPs)

The template-induced synthesis of chemically synthesized transmitters in a polymer is known as molecular imprinting. Specific recognition sites generated by molecular imprinting offer remarkable properties, such as good specificity durability as well as competitive prices, providing compounds tempting substitutes to natural transmitters. Advances in nanotechnology and polymer science have also helped in the performance of screen-printed carbon polymer (MIP) sensing devices. The importance of molecular recognition in biological processes cannot be overstated. It is currently the subject of several studies due to its catalysis and sensing applications. Modern sensor studies aim at developing synthetic receptors that could provide natural interactions between antibodies and antigens, taking both sensitivity and specificity into consideration. The electrochemical deposition process includes creating recognition sites for polymer molecules, which function as templates.

The interaction of the monomer with the template tends to form a cavity around the molecular template; the template is later removed, thus leaving behind the imprinted cavity for target molecular rebinding. The sensor sensitivity has a value of 2.1 W/% RH and an 89 percent repeatability with recovery and response times 155 and 25 s correspondingly. As more than just an outcome, the developed MIP may detect the target analyte preferentially in the template-derived locations [1] [2].

Multi-threading sensors seem to be effective and inexpensive biomolecule sensors. They can be employed in electrical, chemical, optical, and electromechanical monitoring modes [3]. The interaction of an electrolyte and receptors on the surface of an electrode is the basis for electrochemical sensors. In a intriguing study [4]. Microspherical and macroporous MIP particles were immobilized on the surface of a carbon electrode using the sol-gel process, together with graphite (the conducting medium). An alternating heartbeat-modified electrode is utilized as a voltametric method to quantify methylphenidate at concentrations as low as 1 M, yielding findings that are comparable or lower than those reported by electrochemical methods. Another unusual yet intriguing work [5] created an MIP-based duplex novel nucleotide recognition sensor. In one case, a cocaine potentiometric MIP nanoparticle-based sensor was developed [6]. Cocaine is a popular recreational drug; its excessive usage causes symptoms such as internal bleeding, depression, and respiratory arrest, and its use has economic and social ramifications. As a result, it is necessary to develop sensitive and easy cocaine detection technology, especially for either medical or investigative applications. This novel potentiometric biosensor has been built on functionalized polymer nanoparticles (nano MIPs), which are created by a decent optimization phase. A novel potentiometric sensor is built on nanocomposite membrane polymer nanoparticles (nano MIPs) which are created by a solid-phase imprinting process. Nano MIPs manufactured using functional monomer as the acrylamide exhibited the maximum yield and responsiveness to cocaine which is the reason for their choice in device fabrication.

MIP-based optical sensors are classified into two types: (i) MIP affinity sensors and (ii) MIP optoelectronic sensors. For MIP affinity sensors, the devices are capable of detecting analytes possessing properties such as fluorescence, absorbance, and refractive index. For optoelectronic sensors, binding at the analyte/MIP site leads to increased absorbance at a certain wavelength, fluorescence quenching, or a change in refractive index [7][8]. Wren and colleagues [9]

[10] created a fluorescent optical fiber chemical sensor for cocaine. A fluorescent probe for optical fibers was made by synthesizing a rationally selected fluorophore and then incorporating it into a molecularly imprinted polymer. The amount of fluorescence emitted is proportional to the amount of cocaine present in a sample. This sensor is promising with a detection limit of about 1 M, and it takes research in a new direction by providing a rapid and low-cost approach that could be beneficial in drug forensics. Furthermore, they talked about certain MIP-based electrical, chemical, and optical sensing devices, emphasizing their applicability to real-world samples. MIPs moved beyond simple technology demonstrators.

2. Sensors Based on Conducting Polymers

Compounds have been differentiated via their potential to delocalize their pi electrons. Polyacetylene could be turned into a conducting polymer upon doping with Br_2 and I_2 during the first time by MacDiarmid, Shirakawa, and Heeger in 1972 [11][12]. In 2000, this invention was recognized with the Nobel Prize in Chemistry. Conducting polymers provide numerous advantages, including the ability to be doped to display metallic and semiconducting properties. The materials can combine plastic and electrical properties. They may be altered, decomposed in non-polar solvents, and printed using low-cost techniques. However, there are certain disadvantages, such as a lack of long-term stability. They have a wide range of applications due to their characteristics, including supercapacitors, nanocoatings, catalysis, biomedicine, and sensors [13][14]. Polyaniline, polyacetylene (PA), polypyrrole, poly(para-phenylene), and polyfuran were the most often utilized conducting polymers.

Due to their redox activity, this class of polymers is used as a gas detector in sensing. Performance-enhancing drugs can be a p-type or n-type configuration and can change the polymer from a semiconductor to a conducting one. In p-type polymers, the electron migration is from the HOMO-LUMO polymer (chain HOMO) to doping agent LUMO. This transition leads to the creation of polymer holes, causing them to lose electrons. When an oxidized polymer (p-type) is exposed to a reducing agent (CO, NH_3, CH_4, H_2, H_2S, acetone, or ethanol), its resistivity rises; conversely, when the polymer's surface reacts with an oxidizing agent (NOx, CO_2, SO_2, O_2, or O_3), its resistivity reduces [15][16]. The SPE was altered by electrochemically polymerizing polyaniline in HCl. The compiled signal is produced by the reaction of the oxidized polymer substrate ($PANIH^+$) and NH_3; this electron exchange produces an electric flow.

$$PANIH^+ + NH_3 \; PANI + NH_4^+$$

Sensors built of conducting polymers are more accurate than GC/MS. Sensor device assembly should be mechanized, for example, using 3D technology, with a reaction time of a few seconds [17][18]. Forzani et al. [19][20] investigated a glucose oxidase-based electrochemical sensor (GOx). The sensing array is composed of junctions of nano polyaniline, where electropolymerization of monomer takes place in the presence of poly (acrylic acid). GOx increases glucose oxidation to gluconolactone, followed by enzyme degradation to GOx ($FADH_2$). The reduced enzyme combines with the oxygen in the solution, resulting in the formation of GOxFAD and H_2O_2. The conductive polymer is oxidized by peroxide in the last phase.

$$\text{glucose} + \text{GOx(FAD)} \rightarrow \text{gluconolactone} + \text{GOx}(FADH_2)$$

$$\text{GOx}(FADH_2) + O_2 \rightarrow \text{GOx(FAD)} + H_2O_2$$

$$\text{PANIred} + H_2O_2 \rightarrow H_2O + \text{PANIox}$$

Swager et al. [21] assembled a Na^+-based sensor by conducting polymer polythiophene. The first part was carried out by modifying polythiophene with a crown ether. The polymer in an unbound state maintains molecular planarity by distortion of the pi electron cloud. On complex formation with Na^+, there is a twist in the structure because a structure distortion takes place, leading to a decrease in conjugation and conductivity.

The glucose oxidase is then bonded to the polymeric surface. GOx promotes enzyme degradation to GOx($FADH_2$) and oxidation of glucose to gluconolactone. The reaction of the reduced enzyme and oxygen in the solution phase produces GOxFAD and H_2O_2. In the last step, the conductive polymer is oxidized by peroxide [22][23]. The conductivity of the polymer reduces when it is electrochemically oxidized in the presence of Na^+. The impact is likeliest due to the higher inductive action of macrocyclic oxygens [24][25]. To summarize, conducting polymers are widely employed in all types of sensors due to their adjustable electronic properties, simplicity of polymerization, and inexpensive production costs.

3. Sensors Based on Acrylic Polymers

The use of acrylic polymers in sensing is attributed to the sensing functionalities that are covalently bound to the polymeric backbone, which can be tailored to process materials with diverse properties. The commonly used acrylic polymers employed for this purpose are derivatives of acrylamide, their copolymers, and meth/acrylic acid. Various functional groups can be incorporated into acrylic moieties for designing sensor-based materials [26]. Garcia et al. reported acrylic-based sensors with fluorescent/colorimetric properties for various analytes [27][28]. The strategy consisted of thin film polymer preparation by radical polymerization, where 1-vinyl-2-pyrrolidone served as the hydrophilic base, methyl methacrylate (MMA) monomer as the hydrophobic part, and a sensory unit (side group reactive moiety). In one of the works on polymers based on ninhydrin, the evolution of “chronic human wounds” was pictorially represented[29].

The package includes a colorimetric polymer film that changes color when exposed to amino acids. The kit allows for the quantification of total amino acid content by examining the color properties of a sensory film (RGB) acquired from smartphone images. This gadget can aid in the diagnosis of chronic human ailments by providing an analytical procedure that is not influenced by subjective assessment [30][31]. It can create a pH polyacrylate-based sensor where polyacrylic acid (PAA) is obtained utilizing a free radical polymerization approach in aqueous media. The use of ultrasonic energy allows for more robust and environmentally friendly polymerization. PAA is then utilized as a capping agent in the synthesis of AgNPs in the absence of any UV/gamma radiations or any additional reducing agents. Another noteworthy work discussed the creation of an optoelectronic humidity sensor based on Sc(III) polyacrylics [32][33]. To investigate the sorption/desorption of humidity at normal temperature, nanostructured scandium polyacrylate was placed on flat borosilicate substrates. The use of ultrasonic energy allows for more robust and environmentally friendly polymerization. PAA is then utilized as a capping agent in the synthesis of AgNPs in the absence of any additional reducing agents or UV/gamma radiations. The resulting Ag-PA sol was used to detect pH with the naked eye. Another noteworthy work discussed the creation of an optoelectronic humidity sensor based on Sc(III) polyacrylic [34]. To investigate the sorption/desorption of humidity at normal temperatures, nanoscandium-polyacrylate was placed on flat borosilicate surfaces.

4. EVOH Polymers

Because of its barrier qualities against gases and humidity, EVOH is a diblock copolymer consisting of ethylene and vinyl alcohol, which is extensively used in the food packaging and pharmaceutical sectors. When ethylene and vinyl alcohol monomers are copolymerized, the keto–enolic tautomeric balance moves to the aldehydic form, due to which the structure cannot be achieved. As a result, the most often employed synthetic process calls for ethylene and vinyl acetate as monomers, followed by hydrolysis [35].

EVOH is offered on a large scale in various ethylene proportions, viz., 27%, 32%, 38%, and 44%; the variable percentages of monomers result in divergent railing qualities in opposition to gases and solubility in organic solvents. Excess ethylene rates in the formation render the diblock copolymer very hygroscopic and, as a result, with less restraining characteristics when creating hydrogels [6]. It is critical to emphasize that the tacticity and novel functionalities on the polymer’s surface influence its solubility. EVOH is a great contender for sensor development due to its outstanding mechanical characteristics and the simplicity of surface functionalization.

The basis of this sensing approach is the quenching of luminescence by Cu^{2+}. Because nitrogen likeliest correlates with the metal cation, an electron shift from pyrene to Cu^{2+} occurs, encouraging nonradiative relaxation. In the presence of Fe^{3+} and Hg^{2+} in the suspension stage, measurements were purchased. These cations produced a modest level of gleaming quenching. As a result, the suggested approach may be regarded as selective against Cu^{2+} in solution [13].

5. Polymer Inclusion Membranes

Polymer inclusion membranes (PIMs) are liquid membranes based on polymers, invented over 50 years ago, and are employed as the recognizing component of ion-selective electrodes and ocular detectors (optodes). PIMs have recently been used in specimen development and preconcentration, passive sampling, and may be integrated into networked and self-operating devices. A PIM is made of a liquid state and a polymeric brace, which is commonly PVC, cellulose triacetate, or polyethylene glycol (vinylidene fluoride-co-hexafluoropropylene). The polymeric component serves as the membrane’s skeleton, providing mechanical strength. An extractant (carrier) in the liquid phase holds the analyte via ion–couple development or complex formation. Some conveyors have plasticizing properties; however, during membrane production, an extra conditioner is introduced to improve elasticity or increase the solubility of the analyte in the liquid state. PIMs are generally made by liquefying all the ingredients in a tiny amount of evaporative solvent (dichloromethane

or tetrahydrofuran) and diffusing them. The solvent was gently evaporated until a homogenous and clear PIM on the fling surface, which might be level or columnar, was produced. An ion-choosy electrode can be created by casting a film on the tip of the electrode. By including a chromophore in the membrane composition, flat-sheet PIMs may be employed to create optical sensors [36][37]. The gold nanomaterial polymer inclusion membrane was used as a recognizing stage, as well as to immobilize the immunizer. The suggested sensor has the capability for in-place food checks due to its easy investigational technique and the mobility of potentiometric apparatus. The proposed platform's strong performance was proven by an operating span of 1.3–13 × 10^6 cells mL^{-1} and an LOD of 6 cells mL^{-1}, which were equivalent to previous electrochemical label-free immunosensors for ST. The suggested technique may be used for any bacteria–antibody coupling by simply altering the particular antibody and adjusting the AuNP-PIM. For Zn(II) determination, a disposable optode was designed [10]. It is made by immobilizing a dye, 2-acetylpyridine benzoyl hydrazone (2-APBH), in a polymer insertion sheet adhered to the outer side of a polyester band. An investigational factorial blueprint is used to optimize the sheet constitution to get a substance with a pleasing look, as well as appropriate concrete and visual qualities. The best sheet was made of 2.5 g PVC, 4 mL tributyl phosphate, and 40 mg 2-APBH. The optical sensor has a level span of 0.03 (i.e., the LOD) to 1 mg L1 of Zn(II), and it reacts for almost 30 min when submerged in aqueous solutions with a pH of 6. The reactivity to Zn(II) is superior to that of other ordinary cations.

6. Polymer Composites and Nanocomposites

Polymer nanocomposites (PNCs) are formed by the fusion of a polymeric phase (continuous) with a discontinuous phase of nanofillers. Numerous advantages in mechanical, optical, and electrical qualities have piqued the interest of experts all around the world. PNCs may be manufactured in a variety of forms, making them ideal for the development of chemical and biological sensors. Nanostructured polymers have a significant influence on biological and technological fields, particularly in drug delivery, catalysis, and sensing applications [38][39].

Recent breakthroughs in nanotechnology/wearable devices have emerged as significant progress in health care and medical diagnostics, robotic systems, prostheses, visual realities, and professional sports. The use of wearable sensors for the detection of motion and body signals is done by attachment to clothing or fastening to human skin with adhesive straps [40]. An intriguing paper [41] revealed that piezoresistive sensors can be developed as strain sensors employing a copolymer of (styrene butadiene styrene) as the matrix, supplemented with conducting media in the form of carbon nanofillers. Extrusion or spray printing processes were used to create these sensors, which enabled scaling up and inclusion in novel devices.

Graphene is a newly discovered two-dimensional carbon substance. Its clever electrical, optical, and mechanical qualities make it a good candidate for strain sensors. This sensor can detect stretching, bending, and torsion in the human body. The efficient coupling of diverse nanomaterials and conducting polymers with conductive polymers offers new avenues for using PNCs in high-performance biosensing and electrochemical sensing [42].

7. Sensors for Antioxidant Activity

The expected substances for the formation of electrochemical sensors are natural electropolymerized phenolic antioxidants. Electropolymerization of the antioxidants of these substances enables the development of heat-proof polymers. Electro-agile polymeric films capable of functioning as redox-arbitrators and furnishing an electrocatalytic action on the oxidation of organic substances are formed of phenolic antioxidants comprising catechol specks in their composition. To get the extraordinary feedback of the intent analyte, the electropolymerization circumstances need to be optimized. The conduction of innate phenolic antioxidant substances can be accelerated by integrating them with conveying substances such as carbon nano substances, metals, or metal oxide nanomaterials. This perspective has a positive influence on electroconductivity, as well as the efficient outer area of the detector on which polymer electroplating is done. The integration of reformed films elevates the reactivity and specificity of the intent analyte feedback. Moreover, display-imprinted electrodes with already accumulated nano substances of carbon, metal, or oxides of metals can be utilized for restricting polymeric coverage, which is beneficial for day-to-day investigation. This ultimately leads to a decrease in sensor synthesis time, and the analysis procedure. The poriferous shape of polymers offers different advantages, enabling their use as a reactive film of the detector that provides feedback to a broad spectrum of biological and inanimate substances. The polymeric sheets can work as a semipermeable layer, thus allowing the formation of electrochemical detectors for substances of less molecular weight, such as hydrogen peroxide, nitric oxide, and ascorbic acid. The existence of electron-giving atoms in the polymeric layered construction enables it to adhere to heavy metals, furnishing their preconcentration on the outer side of the detector. The perforated setup of the polymeric coverage of organic analytes has the potential to adsorb specimens due to the constructional uniformity and size outcome, specifying both the single or batch reactivity of the detector produced and their broad implementation area in electroanalysis. The

establishment of innate phenolic antioxidants and all antioxidant criteria is of peculiar interest and has a notable experimental perspective.

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